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Methods for the Analysis of Mineral Chromites and Ferrochrome Slag

By D. A. Baker and J. W. Siple

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Information Circular 9240

Methods for the Analysis of Mineral Chromites and Ferrochrome Slag

By D. A. Baker and J. W. Siple

UNITED STATES DEPARTMENT OF THE INTERIOR
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mL	milliliter
g	gram	*N*	normal concentration
h	hour	nm	nanometer
L	liter	pct	percent
meq wt	milliequivalent weight	ppm	part per million
mg	milligram	s	second
min	minute		

METHODS FOR THE ANALYSIS OF MINERAL CHROMITES AND FERROCHROME SLAG

By D. A. Baker[1] and J. W. Siple[2]

ABSTRACT

This report describes the elemental characterization of chromite and related materials at the Bureau of Mines, Albany Research Center. Analytical methods for determining the major constituents, representing extensive experience, refinement, and development, are described and fully annotated. This presentation should allow other laboratories to use these methods and obtain comparable results with a minimum of time needed for familiarization with individual methods.

[1]Research chemist.
[2]Chemist.
Albany Research Center, Bureau of Mines, Albany, OR.

INTRODUCTION

A goal of the Bureau of Mines is the maintenance of an adequate supply of critical minerals and metals to meet national economic and strategic needs. As part of this effort, the Bureau's Albany Research Center has conducted research related to chromium ores and production. In providing analytical support, the Center has analyzed many samples of chromium materials and has acquired considerable experience in the requisite techniques.

Chromium is on the critical materials list because it is widely used in strengthening and enhancing the corrosion resistance of ferrous alloys and there is a lack of adequate domestic resources. In general, the United States has relied on imports to supply 91 pct of its chromium needs, depending on secondary recovery to supply the remaining 9 pct (*1*).[3]

Research projects at the Albany Research Center have ranged from the location and characterization of domestic sources of chromite ore, through smelting ferrochrome ingot operations, to the recovery of chromium and chromium-bearing minerals from various industrial wastes. Reports published include Bureau of Mines Information Circular 8916, entitled "Podiform Chromite Occurrences in the Caribou Mountain and Lower Kanuti River Areas, Central Alaska. Part II: Beneficiation" (*2*) and Bureau of Mines Report of Investigations 8676, entitled "Chromium Recovery From Nickel-Cobalt Laterite and Laterite Leach Residues" (*3*).

In support of these and other research projects, this Center has analyzed a large number of samples of chromite ore, ferrochrome, ferrochrome slag, and solids and solutions from chromium recovery investigations. The large number of samples processed has promoted refinement of the analytical methods used, so that reliability of the results is not sacrificed in order to return the data in a timely manner. The results of this refinement are presented in this publication.

The purpose of this report is to present the techniques used at the Albany Research Center for the analysis of chromite minerals and ferrochrome-related samples. The methods given in this report are based on standard techniques (*4-13*). The presentation is concise and offers supplementary information to aid the understanding of less experienced analysts and technicians. Toward this goal, the format for the presentation of each method includes:

1. A short introductory note on each method.
2. Lists of equipment and materials.
3. A step-by-step listing of the procedure.
4. Procedure notes that provide information pertaining to the reasons for a step in the method or supplementary instructions referring to indications of success, malfunction, or optional actions that may be taken.

The preparation of reagent solutions is presented in appendix A. Appendixes B and C present some notes on the use of zirconium crucibles and on sample preparation.

This format should allow the experienced analyst to take this report into the laboratory and produce results that are comparable and compatible with results obtained at this Center, with a minimum of delay for familiarization with the techniques, and this format should accelerate the understanding of the less experienced analyst.

TOTAL CHROMIUM IN MINERAL CHROMITE AND FERROCHROME SLAGS

The total chromium content in mineral chromite and ferrochrome slags can range from a fraction of a percent in the slags to greater than 30 pct in the ore concentrates. Because of this variation and because of the difficulty in dissolving chromite-containing samples, the method of choice at this Center has been fusion with sodium peroxide, followed by persulfate oxidation and titration with ferrous iron.

The wet method is sufficiently accurate and reproducible for high-quality results on a routine basis. The samples may be determined very rapidly without a sacrifice in quality. Batches of 20 determinations have been completed in 6 h by one analyst without assistance.

Equipment

Zirconium crucible (approximately 30-mL capacity seems most convenient).
Meker or similar gas-air mix burner.
400-mL beaker and cover.
Glass stirring rod.
Hotplate.
Rubber policeman.
Burette.

Materials

Sodium peroxide, reagent grade, granular, 20 mesh or finer.
Sulfuric acid, reagent grade, diluted 1:1 with distilled water.
Saturated manganese solution.
Silver nitrate, reagent grade, 2.5-pct solution.
Ammonium persulfate, reagent grade, crystal.
Hydrochloric acid, reagent grade, concentrated.
Phosphoric acid, reagent grade, concentrated.
Ferrous iron solution, standardized.
Sodium diphenylamine sulfonate solution.

[3]Italic numbers in parentheses refer to items in the list of references preceding the appendixes at the end of this report.

Procedure

1. Weigh the sample into a zirconium crucible.

2. Add 4 to 12 g of sodium peroxide, and stir until the peroxide and sample are thoroughly mixed.

3. Fuse over a burner until all sample particles are dissolved. Swirl and inspect occasionally to keep unattacked particles dispersed.

4. When the fusion is complete, allow the crucible and melt to cool.

5. When they are cool, tap gently to free the solidified melt from the bottom of the crucible.

6. Place the solidified melt and the emptied crucible in a 400-mL beaker, add 150 to 200 mL of cold distilled water, and cover quickly.

7. When leaching activity has subsided, slide the cover aside slightly and slowly add about 25 mL of 1:1 sulfuric acid solution. Reclose the cover and wait for the completion of any further leaching action.

8. Remove and rinse the cover glass, and rinse down the beaker sides.

9. Place a glass stirring rod in the beaker and stir the contents thoroughly.

10. Remove and thoroughly rinse the crucible. Inspect the inside of the crucible and police it if necessary.

11. To the solution in the beaker, add one drop of a saturated manganese solution, 2 or 3 mL of a 2.5-pct solution of silver nitrate, and 3 to 6 g of ammonium persulfate. Stir thoroughly.

12. Bring the solution to a boil, and boil for several minutes to decompose the excess persulfate.

13. Remove the beaker from the hotplate, and immediately add 5 mL concentrated hydrochloric acid to decompose the permanganate.

14. Stir and cool the solution to room temperature or below.

15. When the solution is cool, add about 10 mL of concentrated phosphoric acid, and titrate with a standard ferrous iron solution using two to five drops of sodium diphenylamine sulfonate solution as the indicator, which changes from purple to green at the endpoint.

Titration equation:

$$Cr^{+6} + 3Fe^{+2} \rightarrow Cr^{+3} + 3Fe^{+3}.$$

Calculation:

$$\frac{\text{mL titer} \times N\ Fe^{+2} \times \text{eq wt Cr}}{\text{sample wt} \times 1{,}000} \times 100 = \text{pct total Cr.}$$

$$1\ \text{mL}\ 0.1000N\ Fe^{+2} = 1.733\ \text{mg Cr.}$$

Procedure Notes

1. Sample size is usually roughly calculated to yield a titration of about 20 to 50 mL (as a convenience). However, a minimum of 0.2 g is used when adequate sample is available. A maximum of about 1 g is used to keep the melt volume to a manageable level.

2. Increase the sodium peroxide to match sample size using an approximate ratio of 20 parts of peroxide to 1 part of sample. Again, consideration must be given to melt volume at high sample weights. Thorough mixing cannot be overstressed. Sample particles in the melt can aggregate and stubbornly resist attack.

3. The burner should be capable of bringing the crucible to red heat on the bottom. Mixing remains important. If particles are allowed to aggregate, fusing time may have to be extended, which increases the attack on the crucible itself, shortening its useful life, increasing the tendency of the cooled melt to stick to the crucible, and adding a significant concentration of zirconium to the analyte solution.

4. If the melt is to be leached quickly, the crucible can be set out on any heat-resistant material to cool. If the melt has to be set aside for a while, it should be set on a hotplate on low heat to keep it from absorbing atmospheric water (which makes the melt stick to the crucible).

5-6. If gentle tapping does not free the melt, try moderately hard tapping. If the melt still sticks, lay the crucible on its side in the bottom of the beaker.

7. The leaching reaction can range from very slow to very vigorous. A high aluminum concentration tends to slow the reaction. A slow leach reaction may become a very fast leach reaction when sulfuric acid is added, so care must be exercised. Once the leach reaction has finished, the addition of sulfuric acid is generally accompanied by moderate effervescence unless a significant amount of carbonate is present.

8-10. Rinse down any visible precipitate particles and police out any residue in the crucible. Stirring should produce a clear solution unless hydrolyzed zirconium or aluminum is present. Do not add more sulfuric acid unless iron or chromium hydroxide precipitate is present. Excess sulfuric acid may slow or prevent the oxidation of chromium.

11. The manganese is to indicate the completion of the chromium oxidation. All of the chromium will be oxidized before the manganese begins to be converted to permanganate. If permanganate is the salt added, it may not all reduce and may leave a permanganate pink. Proceed regardless. The permanganate color after the decomposition of the excess persulfate is the important condition, not the pink in the intermediate stages. The silver nitrate is a catalyst in the oxidation reaction. Crystalline ammonium persulfate is used to save the time and labor of preparing fresh solution.

12. When the oxidation is complete and the manganese turns red, it turns quickly, in 1 or 2 s. As the excess persulfate is destroyed, a mild effervescence can be seen in the solution. If the solution does not turn red after boiling for a few minutes, remove it from the hotplate and inspect it for precipitate that looks like silver chloride. If found, add more silver nitrate and ammonium persulfate, and return the solution to the hotplate. If no such precipitate is found, just add more ammonium persulfate, and return the solution to the hotplate. Repeat the operations as necessary. Lost water may be replaced without any hazard to results.

13. The chloride in the hydrochloric acid will be oxidized to chlorine gas in the process of reducing the permanganate. It will also precipitate the silver. The chloride will not react with the dichromate produced.

14. Be aware that a small amount of chlorine gas is evolved during cooling.

15. The phosphoric acid is added to complex the ferric iron. If significant amounts of aluminum or titanium are present, hydrofluoric acid may be substituted for the phosphoric acid. The ferrous iron solution is prepared from ferrous ammonium sulfate in 12-L batches. A piece of purified aluminum sheet kept in the carboy helps to keep the normality of the solution constant. Sodium diphenylamine sulfonate is used because it is easily soluble in distilled water and thus preparation is simplified. Any of the diphenylamine indicators will work, giving a sharp endpoint by changing from purple to green.

ACID-SOLUBLE OR "METALLIC" CHROMIUM IN FERROCHROME SLAGS

At this Center, results from this method have been used almost exclusively as data for the calculation of the total degree of reduction in a smelter batch, rather than as an indicator for the metallization of chromium. When a charge of chromite material is smelted or prereduced, the crystal structure is changed, and once the chromite spinel structure has been opened, the chromium becomes much more available to acid attack. Partially reduced chromium species and chromium in the form of silicates, carbonates, or other carbon compounds, as well as chromium metal, are then available to acid attack. (These species of chromium are often grouped under the name "metallic" chromium.) (It has been noted that a *very* finely ground sample of a mineral chromite concentrate will generally give up a few relative percent of its chromium to this method.)

Equipment

250-mL beaker.
400-mL beaker.
Stirring rod.
Hotplate.
Filter paper.
Funnel.
Burette.

Materials

Sulfuric acid, reagent grade, diluted 1:1 with distilled water.
Hydrofluoric acid, 46 to 51 pct, reagent grade.
Saturated manganese solution.
Silver nitrate solution.
Ammonium persulfate, reagent grade, crystal.
Hydrochloric acid, reagent grade, concentrated.
Phosphoric acid, reagent grade, concentrated.
Ferrous iron solution, standardized.
Sodium diphenylamine sulfonate solution.

Procedure

1. Weigh the sample into a 250-mL beaker.

2. Add 80 to 90 mL of distilled water, 10 mL of 1:1 sulfuric acid, and 5 to 10 mL of hydrofluoric acid.

3. Place the beaker on a hotplate and bring to a gentle boil or just below.

4. Digest at a gentle boil, or just below, for 40 to 50 min, replacing lost water whenever the digestion approaches half the original volume.

5. Remove the solution from the hotplate, cool to about room temperature, and filter through a medium-speed qualitative paper (such as Schleicher and Schuel[4] (S&S) 597) into a 400-mL beaker. Wash 5 to 10 times with distilled water.

6. Dilute the combined filtrate and washes up to 200 to 250 mL total volume.

7. Add one drop of saturated manganese solution, 2 or 3 mL of 2.5-pct silver nitrate solution, and 3 to 6 g of ammonium persulfate, rinse sides, and stir thoroughly.

8. Bring the solution to a boil, and boil several minutes to destroy the excess persulfate.

9. Remove the beaker from the hotplate, and immediately add 3 to 5 mL of concentrated hydrochloric acid to decompose the permanganate.

10. Stir thoroughly, rinse sides, and cool to room temperature or below.

11. When the solution is cool, add about 10 mL of concentrated phosphoric acid and titrate with a standard ferrous iron solution using three to five drops of sodium diphenylamine sulfonate solution as the indicator, which changes from purple to green at the endpoint.

Titration equation:

$$Cr^{+6} + 3Fe^{+2} \rightarrow Cr^{+3} + 3Fe^{+3}.$$

Calculation:

$$\frac{\text{mL titer} \times N\ Fe^{+2} \times \text{eq wt Cr}}{\text{sample wt} \times 1{,}000} \times 100$$

= pct acid-soluble Cr.

1 mL 0.1000N Fe^{+2} = 1.733 mg Cr.

Procedure Notes

1. Sample size is usually roughly calculated to yield a convenient titration. Sample sizes from a few hundred milligrams for prereduced smelter charges up to several grams for slag are easily handled, though large samples of finely ground material sometimes have a tendency to bump.

2. The described acid mixture is proper for all normal determinations. Another small volume of hydrofluoric acid may be added if high silica or metal passivation is suspected. Do not add more sulfuric acid. A high sulfuric acid concentration can slow or prevent the oxidation of chromium from Cr^{+3} to Cr^{+6}.

3-4. Gentle digestion is preferred over vigorous boiling because it requires much less attention and entails less danger of passivating any metallics present.

5. Very fine gangue particles will sometimes pass through ("slime" through) the paper, but they do no harm in the oxidation or titration steps, other than making the solution cloudy.

6. Aim at 150 to 200 mL solution volume at the start of the titration.

7. Saturated manganese solution is to indicate the completion of the chromium oxidation. All of the chromium will be oxidized before the manganese is converted to permanganate. The silver nitrate is a catalyst in the chromium oxidation. Crystalline ammonium persulfate is used to save the time and labor of preparing fresh solution.

8. When the oxidation is complete and the manganese turns red, it turns quickly. As the excess persulfate is destroyed, a mild effervescence can be seen in the solution. If the solution does not turn red after boiling for a few minutes, remove it from the hotplate and inspect it for precipitate that looks like silver chloride. If found, add more silver nitrate and ammonium persulfate, and return the solution to the hotplate. If no such precipitate is found, just add more persulfate and return the solution to the hotplate. Repeat these operations as necessary. Lost water may be replaced without any hazard to results.

9. The chloride in the hydrochloric acid will be oxidized to chlorine gas in the process of reducing the permanganate. It will also precipitate the silver. The chloride will not react with the dichromate.

[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

10. Be aware that a small amount of chlorine gas is evolved during cooling.

11. The phosphoric acid is used as a complexing agent for the ferric iron present. If significant amounts of titanium or aluminum are present, hydrofluoric acid may be substituted for the phosphoric acid. The ferrous iron solution is prepared from ferrous ammonium sulfate in 12-L batches. A piece of purified aluminum sheet kept in the carboy helps to maintain constant normality of the solution. Sodium diphenylamine sulfonate is used because it is easily soluble in distilled water and thus preparation is simplified. Any of the diphenylamine indicators will work, giving a sharp endpoint by changing from purple to green.

TOTAL IRON IN MINERAL CHROMITE AND FERROCHROME SLAGS

Iron is the second major element in chromite. In smelting operations where ferrochrome is the product, a specific range in the chromium-to-iron ratio is desired. Where pure metallic chromium is the product, the iron concentration is not as important. In both cases, it is important to have a good value for the chromium-to-iron ratio. A typical chromite or chromite concentrate can range from less than 10 pct iron to over 20 pct iron.

To cope with this variability and with the difficulty in attacking chromite samples, the method of choice at this Center is titration after alkaline fusion. This method is also used on ferrochrome slags, even though they may occasionally contain less than 1 pct iron.

While this method is not as fast as the total chromium method, rapid and reliable results are easily obtained.

Equipment

Zirconium crucible (approximately 30-mL capacity).
Meker or similar gas-air mix burner.
400-mL beaker and cover.
Glass stirring rod.
500-mL Erlenmeyer flask.
Hotplate.
Funnel.
Filter paper.
Burette.

Materials

Sodium peroxide, reagent grade, granular, 20 mesh or finer.
Hydrochloric acid, reagent grade, concentrated.
Aqueous ammonia, reagent grade, concentrated.
Hydrochloric acid, reagent grade, diluted 1:1 with distilled water.
Stannous chloride, reagent grade, 10-pct solution in 20-pct hydrochloric acid.
Saturated mercuric chloride solution.
Phosphoric acid, reagent grade, concentrated.
Sodium diphenylamine sulfonate solution.
Potassium dichromate, reagent grade, 0.1*N* solution in distilled water.

Procedure

1. Weigh the sample into a zirconium crucible.

2. Add 4 to 12 g of sodium peroxide, and stir until the peroxide and sample are thoroughly mixed.

3. Fuse over a gas and air burner until all sample particles are dissolved. Swirl and inspect occasionally to keep unattacked particles dispersed.

4. When the fusion is complete, allow the crucible and melt to cool.

5. When they are cool, tap gently to free the solidified melt from the bottom of the crucible.

6. Place the solidified melt and the emptied crucible in a 400-mL beaker, add 150 to 200 mL of cold distilled water, and cover quickly.

7. When leaching activity has subsided, remove and rinse the cover and wash down the beaker sides.

8. Slowly, with stirring, add concentrated hydrochloric acid until all the precipitated iron dissolves.

9. Remove and thoroughly rinse the crucible, and police it if necessary.

10. Slowly, with stirring, add concentrated aqueous ammonia until a permanent iron precipitate is obtained; then add 20 to 25 mL excess.

11. Bring the solution to a boil, and boil for a few minutes to destroy any remaining peroxide and produce a more easily filterable precipitate.

12. Remove the beaker from the hotplate, and rinse the sides.

13. Filter the solution through a fast-speed, qualitative paper (such as S&S 595). Wash the beaker once and wash the precipitate three to five times with distilled water, and discard the filtrate and washes.

14. Wash the precipitate back into its original beaker with distilled water.

15. Wash the filter paper free of iron with alternating rinses of hot 1:1 hydrochloric acid and distilled water. Make sure any precipitate particles stuck on the beaker sides are redissolved.

16. Add 20 to 25 mL of concentrated hydrochloric acid, stir until all the precipitate dissolves, and transfer the solution to a 500-mL Erlenmeyer flask.

17. Set the flask on a hotplate and bring it to a boil. Reduce the iron with dropwise additions of 10-pct stannous chloride solution with agitation until the solution is colorless, or light green if Cr^{+3} is present. Add three to five drops excess, and bring to a boil again.

18. Cool the solution to room temperature or below.

19. When the solution is cool, add 10 mL of a saturated mercuric chloride solution, and mix. Immediately add 7 to 10 mL of concentrated phosphoric acid and three to five drops of sodium diphenylamine sulfonate indicator, and titrate with standard potassium dichromate solution to the first permanent purple.

Titration equation:

$$3Fe^{+2} + Cr^{+6} \rightarrow 3Fe^{+3} + Cr^{+3}.$$

Calculation:

$$\frac{\text{mL titer} \times N\ K_2Cr_2O_7 \times \text{eq wt Fe}}{\text{sample wt} \times 1{,}000} \times 100$$

= pct total Fe.

$$1\ \text{mL}\ 0.1000N\ Cr^{+6} = 5.585\ \text{mg Fe}.$$

Procedure Notes

1. Sample size is usually approximated to yield a 10- to 30-mL titration. However, a minimum of about 0.2 g is used when adequate sample is available. A maximum of about 1 g is used to keep the melt volume to a manageable level.

2. An approximate ratio of 20 parts of peroxide to 1 part of sample is used. At high sample weights, resulting melt volume must be considered, however. The flux and sample must be thoroughly mixed, or the sample particles may aggregate and stubbornly resist attack.

3. The burner should be capable of bringing the entire crucible bottom to red heat. Careful agitation must be done to keep the particles from aggregating. Extended fusion time increases the attack on the crucible itself and adds a significant concentration of zirconium to the analyte solution. It also tends to make the cooled melt stick to the crucible.

4. If the melt is to be leached quickly, the crucible can be set out on any heat-resistant material to cool. If the melt has to be set aside for a while, it should be set on a hotplate at low heat to keep it from absorbing atmospheric water.

5-6. If gently tapping does not free the melt, try moderately hard tapping.If the melt still sticks, lay the crucible on its side on the bottom of the beaker.

7-8. The leaching reaction can range from very slow to very vigorous. A high iron concentration speeds the reaction. A high aluminum concentration tends to slow the reaction. A slow leach may become a very fast leach when acid is added. Once the leach is finished, the addition of acid is generally accompanied by mild effervescence unless there is a considerable amount of carbonate present to evolve carbon dioxide.

10. An ammonia precipitation is done to free the iron of the large amount of sodium in the solution and to produce larger precipitate particles. A high sodium concentration has been found to depress the indicator change in the titration. It has also been found that with a sodium hydroxide precipitation, a very fine-grained iron precipitate is produced. The coarser precipitate produced by the ammonia is easily filtered. A small excess of sodium peroxide added to the ammonia precipitation after step 10 will allow the precipitate to be freed of nearly all of the chromium present. Sodium peroxide is added 1 or 2 g at a time until a moderate effervescence is produced by gentle stirring and the beaker contents take on a deeper brown color. Chromium, usually present as hydrated chromic oxide (Cr_2O_3) is oxidized to Cr^{+6} by the sodium peroxide and remains in the filtrate. This operation can be used to measure iron and chromium on the same sample but usually needs to be repeated to remove all visible traces of chromium from the iron solution. If chromium is to be determined, the filtrate is acidified with 1:1 sulfuric acid and titrated as for total chromium. Results are slightly low, and the method is not recommended unless insufficient sample is available for a separate determination.

11-12. Bubbles from peroxide decomposition cause mechanical problems in the filtration, often slowing it unnecessarily.

13. It has been found convenient, after rinsing the beaker, to wash the sides once with hot 1:1 hydrochloric acid from a wash bottle.

15. A glass wash bottle with insulation for holding is used to contain the 1:1 hydrochloric acid for washing.

16. The Erlenmeyer flask is a matter of preference; the titration may be done just as well in the beaker. If a beaker is used, it should be covered during cooling.

17. The stannous chloride reduces the Fe^{+3} to the Fe^{+2} form necessary for the titration. Interfering elements that are reducible by stannous chloride are rare in chromite mineral samples and ferrochrome slags. The excess stannous chloride protects the Fe^{+2} from air oxidation while cooling.

19. Saturated mercuric chloride solution is added in excess to destroy the excess stannous ion; it does not otherwise participate in the titration reaction. Phosphoric acid is added as a complexing agent for Fe^{+3}. If much titanium or zirconium is present in the solution, a gellike precipitate may form when the phosphoric acid is added. This interferes with mixing efficiency and requires a slower and more careful titration. It does not interfere chemically. Hydrofluoric acid may be substituted for the phosphoric acid or added, in small amounts, in addition to the phosphoric acid to avoid this condition. The indicator is at first colorless, turns green as the endpoint is approached (very hard to see when much Cr^{+3} is also present), and sharply turns to purple at the endpoint.

FERROUS IRON IN MINERAL CHROMITE AND FERROCHROME SLAGS

The determination of ferrous iron in mineral chromites and other chromite-bearing samples is limited by the difficult solubility of the chromite lattice. Reaction of the ferrous iron immediately upon release from the crystal seems to be the preferred way of measurement. Attempts to dissolve chromite by other methods depend on strong oxidizing agents that leave no ferrous iron to be measured. The V^{+4}–V^{+5} system is stable enough to yield good results when it is used to react with released ferrous iron.

The situation is complicated, however, by the lack of any standard materials with a certified ferrous iron value. National Bureau of Standards (NBS) 103a chrome refractory, for example, lists an FeO value that is total iron expressed as ferrous oxide. While this value should be fairly close, several relative percent of the ferrous iron are oxidized by atmospheric oxygen in grinding and storage.

With the limitations in mind, researchers at this Center have used results from this method as data for the calculation of smelter charges and of total reduction in a smelter run.

The method requires an overnight digestion, but is otherwise simple and rapid. Reproducibility has been usually within 2 relative percent.

Equipment

150-mL beaker and cover glass.
600-mL beaker.
Stirring rod.
Hotplate.
Pipette (50-mL capacity).
Burette.

Materials

Vanadium-acid mixture.
0.1*N* Fe^{+2} standard solution.
Sodium diphenylamine sulfonate solution.

Procedure

1. Weigh a sample to contain 1.5 meq wt Fe^{+2} or less into a 150-mL beaker.

2. Add just enough distilled water to wet and disperse the sample.

3. Pipette 50 mL of the vanadium-acid mix onto the sample while swirling the beaker to maintain dispersion. Pipette a blank for digestion with each batch of samples.

4. Cover and digest overnight on a hotplate at about 100° C.

5. Remove from the hotplate and cool to room temperature or below.

6. When the solution is cool, slowly pour it into a 600-mL beaker containing 150 to 200 mL of water, while stirring. Thoroughly rinse the small beaker into the large beaker, and dilute the solution to about 500 mL total volume.

7. Titrate with standard Fe^{+2} solution using three to five drops of sodium diphenylamine sulfonate indicator, which changes from purple to green at the endpoint.

Titration equation:

$$V^{+5} + Fe^{+2} \rightarrow V^{+4} + Fe^{+3}.$$

Calculation:

(mL blank titer - mL sample titer) $\times N$ Fe^{+2}

= meq Fe^{+2} in sample.

$$\frac{\text{meq } Fe^{+2} \times \text{meq wt Fe}}{\text{sample wt}} \times 100 = \text{pct } Fe^{+2}.$$

If metallic iron is present, it must be corrected for by subtracting three times the amount of iron present (in milliequivalents) from the milliequivalents of V^{+5} consumed, as in the following equation:

(mL blank titer - mL sample titer) $\times N$ Fe^{+2}

- 3(meq Fe^{o}) = meq Fe^{+2}.

The result is then used in the second equation above.

Procedure Notes

1. Complete solution is more reliably obtained when the sample is limited to 0.5 g or less. Fine grinding is essential to the method, and all samples should be ground to 100 mesh or finer.

2-3. It is necessary to give some attention to maintaining the sample dispersion. The samples have a tendency to form lumps when the acid is added, and this negates the beneficial effects of fine grinding. Lumps of sample stubbornly resist attack.

4. The acid mix will slowly attack glass. Thin or etched beakers should be avoided.

5-6. Take care, this is a very strong acid solution.

7. If metallic iron is present it will consume 3 meq of V^{+5} solution for each milliequivalent of iron present. A separate metallic iron analysis is done, and the results are used to correct the Fe^{+2} results.

METALLIC IRON IN FERROCHROME SLAGS

It would truly be unusual to find a sample of mineral chromite with metallic iron in it. However, this Center has handled many samples of prereduced smelter charges with several percent of metallic iron and ferrochrome slags with measurable quantities of metallic iron. Therefore, this method finds its use in the later stages of mineral chromite processing.

Results from this method have been used to calculate total reduction in smelter runs, the efficiency of the partition of metallics and slag materials, and the final smelter charge.

The method is rapid and reliable and yields high-quality results on a routine basis. Reproducibility has typically been well within 1 relative percent.

Equipment

100-mL volumetric flask with screw cap.
250-mL Erlenmeyer flask.
150-mL beaker.
Hotplate.
Funnel.
Filter paper.
Pipette (50-mL capacity).
Burette.

Materials

Mercuric chloride, reagent grade, crystals.
Hydrochloric acid, reagent grade, concentrated.
Phosphoric acid, reagent grade, concentrated.
Sodium diphenylamine sulfonate solution.
0.1*N* potassium dichromate solution, standardized.

Procedure

1. Weigh the sample into a 100-mL volumetric flask.

2. Using nonmetallic tools, add 8 to 10 g of mercuric chloride.

3. Immediately add 40 to 50 mL of distilled water, and swirl the flask vigorously to mix the contents.

4. Bring the solution to a boil, and boil gently for 1 min.

5. Remove the flask from the heat, and immediately screw the cap on snugly.

6. Cool the solution to room temperature or below.

7. When the solution is cool, dilute to the mark with distilled water, reseal the flask, and mix the contents of the flask thoroughly.

8. Filter into a dry beaker using a dry funnel and a dry, medium-speed qualitative paper (such as S&S 597).

9 Pipette 50 mL of filtrate into a 250-mL Erlenmeyer flask.

10. Add 5 to 10 mL of concentrated hydrochloric acid, 5 to 10 mL of concentrated phosphoric acid, and three to five drops of sodium diphenylamine sulfonate indicator. Titrate with 0.1*N* potassium dichromate solution to a purple endpoint.

Titration equation:

$$3Fe^{+2} + Cr^{+6} \rightarrow 3Fe^{+3} + Cr^{+3}.$$

Calculation:

$$\frac{\text{mL titer} \times N\ Cr^{+6} \times \text{eq wt Fe} \times 2}{\text{sample wt} \times 1{,}000} \times 100$$

= pct metallic Fe.

1 mL 0.1000*N* $K_2Cr_2O_7$ = 5.585 mg Fe.

Procedure Notes

1. A maximum sample size of about 2 g is used to minimize the error caused by solid material in the volumetric flask.

2. Metallic spatulas show definite signs of attack after contact with mercuric chloride; therefore, all handling should be done with glass, plastics, or porcelain utensils, and thorough caution should be used. The final solution after boiling should be saturated with mercuric chloride with a few excess crystals in evidence.

3-6. The mercuric chloride begins attack upon contact with any metal. The attacked metal then becomes much more subject to air oxidation, so delays should be minimized until the solution is boiled and tightly stoppered. Chromium may be taken into solution also, but it does not interfere except by imparting a green color to the solution.

7. Shake the flask until any materials caked on the bottom are thoroughly dispersed. At this point, the flask may be left for up to 24 h before continuing.

8-9. In summary, take a "dry aliquot" of 50 mL into a 250-mL Erlenmeyer flask. Fine materials sometimes slime through the filter paper. They may be ignored unless the filtrate becomes too murky to see the endpoint.

10. The hydrochloric acid provides the proper acid medium for the titration. The phosphoric acid complexes with ferric iron. The endpoint sharply turns to purple. The titrations should be carried out promptly.

ALUMINIUM AND MAGNESIUM IN MINERAL CHROMITE AND FERROCHROME SLAGS

Aluminum and magnesium occur as gangue components in chromite ores and ferrochrome slags. At this Center, ores from many different sites and of many varieties are examined for commercial feasibility. The beneficiation of these ores is a continuing activity that produces most of the samples that are analyzed with this method. Data from this method are used in economic feasibility studies, to decide the best beneficiation methods for different ore types, and to calculate the smelter charge.

The method of choice at this Center is fusion with a minimum of sodium peroxide, solution with hydrochloric acid, and dilution to a proper range for determination by atomic absorption (AA) spectroscopy. This technique is rapid and accurate enough to handle a considerable sample load without sacrificing reliability.

Equipment

Zirconium crucible (approximately 30-mL capacity).
Meker or similar gas-air mix burner.
250-mL beaker
Watchglass to fit 250-mL beaker.
Stirring rod.
100-mL volumetric flask.
Assorted volumetric flasks.
Hotplate.
Rubber policeman.
Assorted pipettes.
AA spectrophotometer.

Materials

Sodium peroxide, reagent grade, granular, 20 mesh or finer.
Hydrochloric acid, reagent grade, concentrated.
Appropriate AA standards.

Procedure

1. Weigh 0.2 g of sample into a zirconium crucible.

2. Add 3 to 4 g of sodium peroxide, and mix thoroughly.

3. Fuse over a burner until all sample particles are dissolved. Swirl and inspect occasionally to keep unattacked particles dispersed.

4. When the fusion is complete, allow the crucible and melt to cool.

5. When they are cool, tap the crucible to dislodge the melt and place the melt in the 250-mL beaker.

6. Add 10 to 20 mL of distilled water to the beaker, and cover quickly with the watchglass.

7. Add about 5 mL of distilled water and 3 to 5 mL of concentrated hydrochloric acid to the crucible.

8. When the leaching action has subsided in the beaker, uncover and rinse the cover and sides with a minimum of distilled water.

9. Police the crucible, and pour the solution slowly into the beaker. Rinse the crucible carefully.

10. Slowly, with stirring, acidify the leach in the beaker with concentrated hydrochloric acid; then add approximately 5 mL excess.

11. Place the beaker on a hotplate at low to medium heat for 15 to 30 min to clarify the solution.

12. Remove the beaker from the hotplate, cool, and transfer the solution to a 100-mL volumetric flask. Make the flask up to the mark and mix.

13. Make a 10:1 dilution of the sample solution for determination of aluminum and a 100:1 dilution for determination of the magnesium.

14. Measure the absorbance of the aluminum at 309.3 nm and the magnesium at 285.2 nm. Set the other AA instrument parameters in accordance with the manufacturer's recommendations.

Procedure Notes

1. Experience has shown that 0.2 g is a convenient amount for nearly all chromite samples.

2. The amount of sodium peroxide used needs to be the bare minimum necessary for reliable sample attack so that the AA instrument will not be overloaded with dissolved salts.

3. The burner should be capable of bringing the crucible bottom to red heat. Mixing is important. If particles are allowed to aggregate, fusing time may have to be extended, increasing the attack on the crucible itself and increasing the tendency of the cooled melt to stick to the crucible.

4. If the melt is to be leached quickly, the crucible may be set on any heat-resistant surface to cool. If the crucible must be set aside awhile after cooling, it should be set on a hotplate on low heat to keep the melt from absorbing atmospheric moisture. Because of its small volume, the melt is usually easier to remove from the crucible if it has solidified with the crucible tilted.

5-10. The small sample and melt size sometimes makes removal of the cooled melt difficult. The higher the iron content, the more vigorous the leach reaction. Police the inside of the crucible thoroughly. When finished, the solution volume should be less than 100 mL.

11. If extended heating was necessary and the crucible attacked, the solution may not clarify because of the presence of hydrolyzed zirconium. (This very rarely happens.)

12. The solution may be left to evaporate if its final volume is greater than 100 mL.

13. A 10:1 dilution will yield a final dilution factor of 1,000:1 for the aluminum. A 100:1 dilution will yield a final dilution factor of 10,000:1 for magnesium. Most samples may then be determined using 10- and 20-ppm standards for the aluminum and 2- and 4-ppm standards for the magnesium.

CALCIUM IN MINERAL CHROMITE AND FERROCHROME SLAGS

Calcium is rarely found in chromite ores in amounts greater than a few tenths of a percent, and calcium analysis is rarely requested on ore samples. Calcium compounds are, however, used as slag conditioners for ferrochrome smelting. Most of the chromite-related samples received for calcium analysis at this Center have been slag samples. The data produced are used mainly to establish material balance in smelter calculations.

The method of choice at this Center is fusion with a minimum of sodium peroxide, solution with hydrochloric acid, and dilution to a proper range for atomic absorption (AA) spectroscopy.

The method for the preparation of the sample for calcium analysis is identical to the preparation of the sample for aluminum and magnesium (previous section). Usually, the dilution prepared for aluminum is a proper concentration for calcium determination using 2- and 5-ppm calcium standards. Occasionally, the dilution prepared for the magnesium determination is used when the calcium concentration is high. The undiluted solution (step 12 of the aluminum-magnesium method) is used when the calcium concentration is low. When analyzing for calcium, a reagent blank must be carried along to correct for the calcium content of the sodium peroxide. Better precision is obtained if the sodium peroxide flux is weighed when preparing the fusions for calcium analysis.

The absorbance of the calcium solution is measured at 211.3 nm with the other AA instrument parameters set according to the manufacturer's recommendations. When calcium determination is combined with the determination of aluminum and magnesium, samples may be run rapidly and large sample loads may be analyzed quickly without sacrificing reliability.

GRAVIMETRIC SILICA IN MINERAL CHROMITE AND FERROCHROME SLAGS

Silica is present in chromite ores as a basic silicate. In characterization and beneficiation studies performed on chromites at this Center, the chromium-silica ratio determines the purity of the gangue material being analyzed. Accurate characterization of the original ore material and the further feasibility of smelting to ferrochrome are identified by using this ratio.

The method of analysis for silica at this Center is dehydration of the silicic acid with sulfuric and perchloric acids. One dehydration is accurate enough for characterization of the ore.

Equipment

Zirconium crucible (approximately 30-mL capacity).
Platinum crucible (approximately 20-mL capacity).
Meker or similar gas-air mix burner.
400-mL beaker and cover.
Boiling or bump cup for 400-mL beaker.
Glass stirring rod.
Hotplate.
Rubber policeman.
Funnel.
Filter paper and pulp.
Fume cabinet or hood suitable for the fuming of perchloric acid.
Muffle furnace.

Materials

Sodium peroxide, reagent grade, granular, 20 mesh or finer.
Hydrochloric acid, reagent grade, concentrated.
Sulfuric acid, reagent grade, diluted 1:1 with distilled water.
Perchloric acid, reagent grade, concentrated.
Hydrofluoric acid, reagent grade, 48 to 51 pct.
Hydrochloric acid, reagent grade, diluted 20:1 with distilled water.

Procedure

1. Weigh 0.5 g of the sample into a zirconium crucible.

2. Add 4 to 12 g of sodium peroxide, and stir until the sample is thoroughly mixed.

3. Fuse the crucible contents using the gas and air burner until all particles are dissolved completely.

4. When the fusion is complete, allow the crucible and its contents to cool.

5. Gently tap the melt into a 400-mL beaker, and add 50 to 75 mL of distilled water.

6. Carefully add to the crucible 10 to 15 mL of distilled water and 5 mL of concentrated hydrochloric acid. When the chemical action ceases, slowly pour the contents of the crucible into the 400-mL beaker containing the main melt.

7. Police the crucible, being careful to remove any adhering silica particles from the sides.

8. Acidify the solution in the 400-mL beaker with concentrated hydrochloric acid.

9. To the beaker add 30 mL of 1:1 sulfuric acid and 40 mL of concentrated perchloric acid.

10. Place the beaker and its contents on a hotplate in a *perchloric acid hood*, and slowly evaporate the solution until dense white fumes of perchloric acid appear.

11. Put a cover glass over the beaker, and reflux at a high-heat setting on the hotplate for 15 to 20 min. A boiling or bump cup made of aluminum or similar material helps avoid splattering.

12. When the beaker is cool, add 150 mL of distilled water to the mass in the beaker and stir. Slightly heat, if necessary, to dissolve any insoluble material other than the silica.

13. Filter the solution through a medium-speed paper (such as S&S 589 white ribbon) plus a little paper pulp, and police the 400-mL beaker to remove any silica that adheres to the sides.

14. Wash the silica caught in the filter paper, alternately, five times with distilled water and five times with the 5-pct hydrochloric acid wash solution (heat slightly).

15. After allowing the filter paper and its contents to drain properly, place them in a clean platinum crucible.

16. Starting at a low temperature in a muffle furnace, ignite the crucible and contents to 1,200° C for approximately 1 h.

17. Cool in a desiccator, and weigh the platinum crucible containing the ignited silica and its associated impurities.

18. Add 3 to 5 mL of hydrofluoric acid and one to two drops of 1:1 sulfuric acid to the platinum crucible.

19. Slowly volatilize the silica as silicon tetrafluoride on a hotplate at a low heat.

20. As soon as the hydrofluoric acid and silica have evaporated and fumes of sulfuric acid appear, increase the hotplate temperature to a high setting.

21. When drying is complete, ignite the platinum crucible and impurities to a red heat over a burner.

22. Weight the platinum crucible and impurities when cool.

Calculation:

$$\frac{(\text{wt Pt crucible} + \text{SiO}_2 + \text{impurities}) - (\text{wt Pt crucible} + \text{impurities})}{\text{sample wt}} \times 100 = \text{pct total SiO}_2.$$

Procedure Notes

1. A sample size suitable for most chromite ores is 0.5 g. If considerable (over 40 pct) silica is present, reduce the sample size to 0.25 g.

2. Increase the sodium peroxide as the sample size increases, at an approximate ratio of 20 parts of peroxide to 1 part of sample. Again, however, consideration must be given to melt volume at high sample weights. Thorough mixing cannot be overstressed. Sample particles in the melt can aggregate and stubbornly resist attack.

3. The burner should be capable of bringing the crucible to red heat on the bottom. Mixing remains important. If particles are allowed to aggregate, fusing time may have to be extended, which increases the attack on the crucible itself, shortening its useful life, increasing the tendency of the cooled melt to stick to the crucible, and adding a significant concentration of zirconium to the analyte solution.

4. If the melt is to be leached quickly, the crucible can be set out on any heat-resistant material to cool. If the melt has to be set aside for a while, it should be set on a hotplate on low heat to keep it from absorbing atmospheric water (which makes the melt stick to the crucible).

5. If gentle tapping does not free the melt, try moderately hard tapping. If the melt still sticks, lay the crucible on its side in the bottom of the beaker.

6. The leaching reaction can range from very slow to very vigorous. A high aluminum concentration tends to slow the reaction. A slow leach reaction may become a very fast leach reaction when sulfuric acid is added, so care must be exercised. Once the leach reaction has finished, the addition of sulfuric acid is generally accompanied by moderate effervescence unless a significant amount of carbonate is present.

7. Using glassware will introduce negligible silica into the analysis, although one must be careful not to unintentionally add silica by accidentally chipping a stirring rod, etc. Carefully police all glassware and crucibles to remove particles of silica. Nonignited silica is quite sticky and adheres readily to most surfaces.

9. The purpose of using sulfuric and perchloric acids is to dehydrate the soluble silicic acid $SiO_2 \cdot H_2O$ to insoluble silica (SiO_2). These two acids are excellent for this purpose.

10. A special perchloric acid hood is needed for evaporation since most commercial hoods are not designed for this purpose and may react explosively to perchloric acid fumes.

11. When the solution reaches a volume of approximately 100 to 125 mL, salts start to precipitate. As this happens, occasional stirring keeps the solution well mixed and prevents bumping. A bump or boiling cup is a good preventative measure against splattering.

12. An acid volume of 50 to 75 mL is satisfactory for refluxing to begin. Do not fume off all of the perchloric acid. If this happens, insoluble chromium salts will appear, which will not redissolve upon adding water. Should this occur, add more perchloric acid and refume. Refluxing for

15 to 20 min removes almost all of the water from the silicic acid and also oxidizes the iron and chromium in solution to an orange color.

13. After adding distilled water to the cooled and refluxed silicic acid, do not let the solution stand for long, as some of the colloidal silica will redissolve. It may be necessary to heat the beaker and its contents slightly or to add several milliliters of concentrated hydrochloric acid to redissolve any material that is difficult to dissolve.

14. Wash the filter paper carefully to remove all traces of perchloric acid. *If this is not done, the remaining perchlorates will ignite explosively in the furnace.*

16. The ignition to 1,200° C effectively removes all traces of water from the silica.

17. Ignited silica (SiO_2) is light and fluffy. Avoid air drafts and spillage when weighing and igniting. The weighed silica is always impure, and with chromites it may have a light greenish color. Impurities include aluminum, chromium, iron, titanium, vanadium, and zirconium, as well as beryllium, calcium, and strontium, if present in the initial material. The weight of impurities should be extremely small in comparison to the weight of silica obtained if the analysis is carefully done.

18. Adding hydrofluoric acid to the weighed silica produces silicon tetrafluoride (SiF_4), which is a gas. *This step must be done in a hood as fumes of hydrofluoric acid and silicon tetrafluoride are extremely toxic.* Sulfuric acid also must be added to the platinum crucible containing the ignited silica and impurities. When the platinum crucible is reignited with its residue of iron, aluminum, etc., everything remaining will be reignited to an oxide form, as originally done at 1,200° C rather than to a fluoride form. As an example, ferric sulfate [$Fe_2(SO_4)_3$] as an impurity in the platinum crucible is converted to ferric oxide (Fe_2O_3) and sulfur trioxide (SO_3) upon reignition.

21. Dirty platinum crucibles may be cleaned by fusing sodium bisulfate in them until the sides and bottom are free of stuck particles.

MANGANESE IN MINERAL CHROMITE, FERROCHROME SLAGS, AND FERROCHROME

Manganese commonly occurs in mineral chromite as an impurity, and the amount can range from trace quantities to a few percent. In ferrochrome smelting operations, the manganese should find its way into the slag rather than the metal. Data from these analyses have most often been used to trace the partitioning of the manganese through the smelting process and for material balance calculations.

At this Center, the method of choice for slags and ores is decomposition by peroxide fusion, followed by a separation of interfering elements and oxidation of the manganese to permanganate, to be measured by molecular absorbance in an ultraviolet- (UV) visible spectrophotometer.

Metallic ferrochrome samples may be decomposed by fusion if the sample is ground to 100 mesh or finer and the sodium peroxide flux is moderated by the addition of 10 to 20 pct of sodium carbonate. Acid digestion beginning with approximately 5-pct sulfuric acid and a trace of hydrofluoric acid is the alternative.

Equipment

Zirconium crucible (approximately 30 mL capacity).
Meker or similar gas-air mix burner.
150-mL beaker.
250-mL beaker and cover.
Stirring rod.
Magnetic stirrer and stirring bar.
200-mL volumetric flask.
100-mL volumetric flask.
Rubber policeman.
Funnel.
Filter paper.
Assorted pipettes.
UV-visible spectrophotometer.
Wash bottle.

Materials

Sodium peroxide, reagent grade, granular, 20 mesh or finer.
Sodium carbonate, reagent grade, anhydrous powder.
Sulfuric acid, reagent grade, diluted 1:1 with distilled water.
Hydrogen peroxide, reagent grade, 30-pct solution.
Zinc oxide, reagent grade, slurry.
Iodate oxidant solution.
Standard manganese solution.

Procedure

1. Weigh the sample into a zirconium crucible.

2. Add 5 to 10 g of sodium peroxide (plus 1 to 2 g of sodium carbonate for ferrochrome metal), and stir until the sample and flux are thoroughly mixed.

3. Fuse over a burner until all sample particles are dissolved. Swirl and inspect occasionally to keep unattacked particles dispersed.

4. When the fusion is complete, allow the crucible and melt to cool.

5. When they are cool, tap gently to free the melt from the bottom of the crucible.

6. Place the solidified melt in the 250-mL beaker, add about 20 mL of distilled water, and cover immediately.

7. Place the crucible in front of its beaker, and add to the crucible about 5 mL of distilled water and about 2 mL of 1:1 sulfuric acid.

8. Police the crucible thoroughly, and slowly rinse its contents into the beaker with a small amount of distilled water.

9. Remove and rinse the beaker cover and the beaker sides. Place a stirring rod in the beaker.

10. Slowly and with vigorous stirring, acidify the leach in the beaker with 1:1 sulfuric acid.

11. Add 30-pct hydrogen peroxide dropwise with vigorous stirring to reduce the Cr^{+6} to Cr^{+3} and bring the beaker to a boil to decompose any excess peroxide.

12. When the solution is clear, remove from the hotplate and cool to room temperature.

13. Place a stirring bar in the beaker and begin stirring at a moderate rate.

14. Add zinc oxide slurry in small (3- to 5-mL) portions, allowing for dispersion between additions, until all iron and chromium are precipitated and a small excess of zinc oxide is apparent.

15. Remove and rinse the stirring bar, and transfer the sample slurry to a 200-mL volumetric flask. Use a wash bottle to ensure complete transfer.

16. Cool to room temperature and make up to volume with distilled water. Stopper, mix, and let settle for a time.

17. Using a dry funnel, dry paper, and a dry beaker, filter a portion of the supernatant liquid through a medium-speed qualitative paper (such as S&S 597).

18. Pipette an aliquot of dry filtered solution into a 150-mL beaker.

19. Add 20 mL of the iodate oxidant solution, and set the beaker on a hotplate at low to medium heat.

20. Leave the beaker on the hotplate for about 15 min after the first appearance of the permanganate purple.

21. Remove the beaker from the hotplate, and cool to room temperature.

22. Transfer the solution to a 100-mL volumetric flask, make to the mark with distilled water, stopper, and mix.

23. Measure the absorbance of the solution with a UV-visible spectrophotometer at 545 nm.

24. Prepare a calibration curve by pipetting appropriate aliquots of a standard manganese solution into 150-mL beakers and following steps 19 through 23.

Procedure Notes

1. Sample size is estimated to yield 0.5 to 1 mg of manganese in the *final aliquot* for oxidation.

2. Increase the sodium peroxide as the sample size increases, but consider the final melt volume when the sample weight approaches 1 g. When metals are fused in sodium peroxide they tend to behave like a thermite mixture. Carbon will behave that way also but will not get as hot as a metal. The addition of sodium carbonate to the flux will slow the reaction of metal and peroxide. Iron burns very fast and very hot; chromium burns much more slowly. If a sample of ferrochrome were as high as 80 pct chromium, moderation with sodium carbonate would probably not be necessary as long as the sample and flux were well mixed. Efficient mixing of the sample and flux cannot be overemphasized. Several milligrams of sample left unmixed can produce a spot hot enough to burn through a zirconium crucible.

3. The burner should be capable of bringing the bottom of the crucible to red heat. When the flux and sample reach sintering temperature, sample particles may begin to burn. This produces reddish-orange flashes and some hissing and popping sounds. When this happens, remove the crucible from the flame and attempt to swirl the contents so that the heat of the burning metal will be absorbed by the remaining flux and sample mix. This is called autofusion and is common in samples with a very

high carbon content and well-moderated flux. Rarely will any of the sample-flux mixture be ejected from the crucible if mixing has been thorough. Very rarely a sample-flux mix will "skyrocket" or be uncontrollably active. If this happens, while holding the crucible with tongs, remove the crucible from the flame and hold it as still as possible until the activity has subsided. Let the melt solidify and drop the crucible into a large beaker or sink partly filled with tap water. Spilled melt may sometimes be chipped off such materials as transite and stone counters, but thorough cleanup will require the use of dilute acid and plenty of water. Skyrocketing is nearly always caused by inaccurate sample estimates, very poor mixing of sample and flux, or lack of flux moderation; with care it is avoidable.

4. If the melt is to be leached soon, then the crucible may be placed on any heat-resistant material to cool. If the melt must sit for some time before leaching, the crucible can be placed on a low-heat hotplate to keep it from absorbing atmospheric moisture.

5-6. If gentle tapping does not free the melt, then stronger tapping should be tried. If the melt sticks stubbornly, then place the crucible upside down on a clean piece of some durable, nonbrittle, nonreactive material (such as a clean scrap of counter stone). Tap on the bottom of the crucible with a light hammer until the melt is broken free. Transfer the melt to a 250-mL beaker, and rinse any small melt particles into the beaker also. Proceed with the leach.

7-8. Often a small part of the melt will stick in the crucible bottom, and the melt will splatter on the crucible walls during fusion. These walls should all be policed. Pour the policing solution into the beaker slowly and carefully. The solution in the beaker is very basic, and the solution in the crucible is moderately acidic.

9. The leaching reaction is usually quite active and often splashes leachate on the cover and sides.

10. Considerable heat is evolved when acidifying the highly basic leachate with the highly acidic 1:1 sulfuric acid. Excess sodium peroxide will also be partially decomposed and give off oxygen. Vigorous stirring and slow acid addition are therefore imperative. Observe closely during the acid addition to keep the reaction from boiling out of the beaker. If sodium carbonate was added to the flux, then carbon dioxide will be evolved on acidification, causing considerable foaming and requiring even closer attention.

11. Ideally, just enough acid should be added to completely dissolve the melt. Practically, attempt to keep the excess of acid small; it will be neutralized in a later step. The solutions resulting from fused samples usually have most, if not all, of their chromium in the +6 state. It is necessary to reduce this chromium to the +3 state so that it will be precipitated by the zinc oxide since the Cr^{+6} will interfere in the absorbance measurement. The most often used method of reducing the Cr^{+6} to the Cr^{+3} state is to add small portions of 30-pct hydrogen peroxide until an addition produces no color change and little more effervescence. The solution is then boiled for several minutes to destroy excess peroxide. The addition of hydrogen peroxide to an acidic solution of Cr^{+6} first produces the purple Cr^{+5} ion, which then disproportionates to Cr^{+3} and Cr^{+6}. This purple color is very intense; lack of it, upon a peroxide addition, is the prime indicator of complete reduction. Boiling will decompose excess hydrogen peroxide, but a small amount remains intact. This excess peroxide will consume the oxidizing solution by reacting with the oxidized manganese. Therefore, close attention must be given during the Cr^{+6} reduction to minimize the hydrogen peroxide excess.

12. The zinc oxide precipitation will cause heat to be evolved, so the solution should be cooled.

13-15. Stirring should be vigorous enough to completely disperse the added zinc oxide slurry but not vigorous enough to cause bubbles. For the best results, allow the first few additions to dissolve completely before continuing. When the precipitate becomes dark and begins to persist, make the additions slightly larger and more frequent until the precipitate no longer darkens but begins to lighten in color. The precipitation is complete when there are white particles of zinc oxide visible in the precipitate and the liquid looks slightly milky if the precipitate is allowed to settle for a minute or two.

16. When mixing the contents of the flask, shake vigorously enough to dislodge from the glass any precipitate that has caked while cooling.

18. Take an aliquot to approximate a manganese content of 1 mg if possible, but use 50 mL as a maximum.

20. All of the manganese present should be oxidized within 5 min of the first appearance of color; 15-min digestion allows a safety factor.

23. Measurements should be made the same day as the oxidation step. Checks made at this Center have indicated that the color is stable for at least 24 h, except in the case of very high manganese concentrations (more than 3 mg of manganese per 100-mL flask).

ACID DIGESTION OF FERROCHROME METAL

At times it may be necessary or desirable to dissolve a ferrochrome sample in acid rather than fusing it in sodium peroxide. Acid digestion methods are slow, but require little in the way of attention. Two alternative methods are described here. The A method is the basic method to use for most ferrochrome samples. The B method is for very stubborn samples.

METHOD A

Equipment

250-mL beaker and cover.
400-mL beaker and cover.
Hotplate.
Funnel (optional).
Filter paper (optional).
Fume hood.

Materials

Sulfuric acid, reagent grade, 5-pct solution.
Hydrofluoric acid, reagent grade, concentrated.

Procedure

1. Weigh the sample into a 250-mL beaker.

2. Add 100 mL of 5-pct sulfuric acid solution and 1 to 2 mL of concentrated hydrofluoric acid.

3. Place the beaker on a low- to medium-heat hotplate, and cover.

4. When the sample has dissolved, remove the cover and take the solution to fumes of sulfuric acid; allow it to fume for a few minutes.

5. Remove the beaker from the heat, cool, and dilute with distilled water. Warm if necessary to redissolve the salts.

6a. If the sample is for a total chromium determination, transfer the solution to a 400-mL beaker and go to step 11 of the total chromium method.

6b. If the sample is for total iron determination, transfer the solution to a 400-mL beaker, add 3 to 5 g of ammonium chloride, and go to step 10 of the total iron method.

6c. If the sample is for manganese determination, cool to room temperature or below and go to step 13 of the manganese method.

Procedure Notes

2. The acid digestion must be started gently. If the initial acid concentration is too high, the chromium in the ferrochrome will be passivated or become very unreactive. The low initial sulfuric acid concentration and the addition of the small amount of hydrofluoric acid are to avoid this passivation.

3. The solution will slowly lose water; do not allow the total volume to drop below about 25 mL until all of the sample has dissolved.

4. Do not take the solution to copious fumes or allow it to fume for more than a few minutes. Excess fuming can form refractory chromium salts that are as difficult to dissolve as chromite itself.

6. The solution may contain carbon or precipitated silica. To remove them, if desired, filter the solution through a medium- to slow-speed qualitative paper and wash thoroughly.

METHOD B

Equipment

250-mL beaker and cover.
400-mL beaker and cover.
Hotplate,
Funnel (optional).
Filter paper (optional).
Perchloric acid fume hood.

Materials

Perchloric acid, reagent grade, concentrated.
Nitric acid, reagent grade, concentrated.

Procedure

1. Weigh the sample into a 250-mL beaker.

2. Add enough water to just cover the sample and 25 mL of perchloric acid.

3. If the sample is known to have a high carbon content, add 20 mL of concentrated nitric acid.

4. Cover the beaker and set on a medium- to high-heat hotplate.

5. Bring to fumes of perchloric acid, and fume, covered, until all metal particles are dissolved.

6. See step 6 of method A.

Procedure Notes

3. Nitric acid is necessary only when carbon is present in percent amounts. The nitric acid partially oxidizes the carbon so that when the perchloric acid begins to react with it the carbon does not react explosively. Carbon that has not been predigested with nitric acid will often react explosively when the perchloric acid reaches fuming temperature.

4-6. The sample is attacked by fuming perchloric acid to produce chromic acid. The process is slow, and the cover is necessary to provide some reflux. Chromic acid crystals are usually produced, and it may be necessary to cool the beaker and dissolve the crystals with water to see if the last particles of sample have dissolved. Silica is precipitated by the fuming perchloric acid and may be visible as light-colored, low-density particles in the solution. Carbon is oxidized to carbon dioxide by the fuming acid, but occasionally graphite will survive the treatment. If graphite is present, it will usually be found floating on the surface of the solution and occasionally as dark-colored, low-density particles on the bottom. Unattacked sample will be the only heavy or high-density particles in the beaker. If no heavy particles can be seen, then the solution is considered complete. If the sample is to be used for a manganese determination, the chromium should be reduced to the +3 state. (See step 11 of the manganese method.) If removal of the perchloric acid is desired, this can be done by adding 20 mL of 1:1 sulfuric acid and taking it to fumes.

DISCUSSION

Analysts assigned to make a new determination on a sample often must deduce the significance of steps in the usually sketchy procedure descriptions of in-house methods and methods in journal or reference publications. The familiarization process results in a delay in mastering the method. This report seeks to shorten that delay, allowing analysts newly assigned to the covered determinations a quicker understanding of the methods.

The information presented here was collected empirically by the analysis of thousands of samples over several years and the observation of the effects of small variations in technique.

The reliance on zirconium crucibles as alkaline fusion vessels may have been noted. Their reliability in terms of durability and lowered introduction of interfering species in comparison to iron and nickel crucibles has been proven to the satisfaction of this Center. They should not, however, be used in fusions in a muffle furnace because of significant oxygen attack.

Any request for assistance concerning the subject of this report should be addressed to the authors, Bureau of Mines, Albany Research Center, Albany, OR.

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APPENDIX A.--REAGENT PREPARATION

0.1N Fe^{+2} Solution

Preparation

Dissolve 39 g of ferrous ammonium sulfate hexahydrate in distilled water with 10 mL of concentrated sulfuric acid. Dilute to 1 L with distilled water.

Standardization

Weigh accurately 130 to 140 mg of primary standard-grade potassium dichromate into each of three 400-mL beakers. Add about 150 mL of distilled water and about 5 mL of concentrated sulfuric acid, and stir until completely dissolved. Titrate with the new ferrous solution to the disappearance of the diphenylamine sulfonate indicator purple.

Calculation

$$N\ Fe^{+2} = \frac{\text{wt } K_2Cr_2O_7 \times \text{pct purity } K_2Cr_2O_7}{\text{meq wt } K_2Cr_2O_7 \times 100 \times \text{mL titrated}}.$$

$$\frac{\text{mg Cr}}{\text{mL } Fe^{+2}} = \frac{N\ Fe^{+2} \times 51.996}{3}.$$

$$1\text{ mL } 0.100N\ Fe^{+2} = 1.733\text{ mg Cr.}$$

0.1N Cr^{+6} Solution

Preparation

Dissolve 4.9 g of potassium dichromate in distilled water and dilute to 1 L.

Standardization

Weigh accurately 0.17 to 0.18 g of electrolytic or NBS standard-grade iron metal into each of three 250-mL beakers. Add 20 mL of distilled water and 20 mL of concentrated hydrochloric acid, cover, and heat gently until the iron is completely dissolved. When dissolved, remove from the heat. Remove the cover, and rinse any condensate into the beaker. Rinse the beaker sides, and quantitatively transfer the solution to a 500-mL Erlenmeyer flask. Make the volume up to 125 to 150 mL with distilled water. Bring to a boil and, dropwise, add 10-pct stannous chloride solution, with mixing, until the solution is colorless. Add 3 to 5 drops excess and just bring to a boil again. Cool to room temperature or below, and add 10 mL of a saturated solution of mercuric chloride: mix, and add 10 mL of concentrated phosphoric acid. Titrate with the prepared Cr^{+6} solution using sodium diphenylamine sulfonate indicator to a purple endpoint.

Calculation

$$N\ Cr^{+6} = \frac{\text{wt Fe} \times \text{pct purity Fe}}{\text{meq wt Fe} \times 100 \times \text{mL titrated}}.$$

$$\frac{\text{mg Fe}}{\text{mL } Cr^{+6}\text{ sol'n}} = N\ Cr^{+6} \times 55.847.$$

$$1\text{ mL } 0.1000N\ Cr^{+6} = 5.585\text{ mg Fe.}$$

Sodium Diphenylamine Sulfonate Indicator

Dissolve 1.35 g of reagent-grade sodium diphenylamine sulfonate in 500 mL of distilled water.

Vanadium-Acid Mixture for Ferrous Iron

Add 3.0 g of vanadium pentoxide (V_2O_5) to a mixture of 300 mL of concentrated phosphoric acid and 600 mL of concentrated sulfuric acid. Heat and stir until all of the vanadium pentoxide has dissolved. Add, dropwise, a saturated solution of potassium permanganate until the acid mixture gives a faint pink when a few drops are diluted with water. Heat to fumes of sulfuric acid, and continue to fume for several minutes to destroy the excess permanganate. Cool thoroughly and transfer to a stock bottle. If filtration is necessary, use a pad of glass wool in a large funnel.

Silver Nitrate Solution

Dissolve 25 g of reagent-grade silver nitrate in distilled water and 10 mL of concentrated nitric acid. Dilute to 1 L and store away from light.

Stannous Chloride Reducing Solution

Dissolve 20 g of stannous chloride in 200 mL of 20-pct (1:4) hydrochloric acid. Make this solution fresh weekly or store it in a bottle with several high-purity tin shot.

Saturated Mercuric Chloride Solution

Heat distilled water in a large beaker to almost boiling. Add reagent-grade mercuric chloride to the water by the spoon or spatula with vigorous stirring until no more will dissolve. Transfer to a stock bottle.

Manganese Oxidant Solution

Dissolve 7.5 g of reagent-grade potassium periodate in 100 mL of hot 1:1 nitric acid. When dissolved, cool and add 400 mL of concentrated phosphoric acid, dilute to 1 L, and transfer to a stock bottle.

Saturated Manganese Solution

Nearly fill a convenient size stock bottle with warm distilled water. Add manganese sulfate or potassium permanganate to the bottle, and shake or stir until dissolved. Repeat until no more will dissolve, and add a small excess. Transfer a portion of the supernatant liquid to a dropping bottle for use. Replenish the water or the manganese compound as necessary.

Zinc Oxide Slurry

Half fill a 250-mL beaker with zinc oxide powder. Add distilled water with stirring until the slurry is smooth and is the consistency of heavy cream or heavy latex paint. Stir the slurry occasionally during use.

APPENDIX B.–USE OF ZIRCONIUM CRUCIBLES

Zirconium crucibles are rapidly becoming a standard piece of equipment, particularly in laboratories where fusions using strongly alkaline fluxes are common. This Center has found no better material to use for the thousands of sodium peroxide fusions that are done here every year.

Zirconium crucibles usually arrive from their suppliers in a polished, silvery state. They resemble a polished iron or nickel crucible very closely. If they become confused with iron or nickel crucibles, they can be identified by tapping them with a pencil or spatula and listening to the tone produced. Zirconium crucibles produce a pleasant, almost musical tone when tapped. The first use of the crucible in a flame will produce a dark-gray coating over the metal that seems to enhance the crucible's resistance to sodium peroxide. It is thought that this coating is a nitride or a nitride-oxide mixture, but no attempt has been made to confirm or refute the idea.

The use of zirconium crucibles should be limited to alkaline fluxes and fusions done over a burner. Zirconium crucibles should not be used for extended fusions or ignitions in a muffle furnace unless an atmosphere free of nitrogen and oxygen can be maintained in the furnace. The hottest part of the flame produced by a Fisher or similar design gas-air mix burner is proper for most sample-flux mixtures. If a high carbon, sulfide, or metallic content sample is being fused, it is usually desirable to begin the fusion gently in case the sample goes into autofusion. The crucible may be supported on a wire triangle over the flame or held with tongs, depending on the analyst's preference.

Autofusion occurs when the sample-flux reaction is exothermic, and the effect can range from barely detectable to explosive. Any sample known to contain a reduced species or a reducing agent should be fused in sodium peroxide moderated by the addition of anhydrous sodium carbonate, and extra care must be taken in assuring complete mixing of the sample and flux. A well-mixed fusion will seldom eject material from the crucible even if the fusion becomes quite active. If an autofusion becomes too active or skyrockets, remove the crucible from over the burner as quickly as safety will allow. Place or hold the crucible with tongs where it will not contaminate any other work, until the melt solidifies, and then drop the crucible into a large beaker or a sink partially filled with water. Allow the leaching reaction to subside and then retrieve the crucible, clean it, and check it for damage.

With proper care, zirconium crucibles can last for more than 100 fusions. They should be checked before their first use for manufacturing flaws such as cracks or pits. During normal use, the bottom of the crucible is the part that receives the most severe abuse and the edge of the bottom is where most crucibles fail. As the crucible is used the bottom becomes thinner, and when it is thin enough so that it can be flexed with finger pressure, the crucible should be checked before each use for pinholes around the edge of the bottom. Discard any crucible that has a pinhole; the thin edge of a pinhole is particularly susceptible to attack by sodium peroxide. Also, do not use crucibles with thin bottoms to fuse samples that may autofuse. Extending the fusion time for a sample increases the attack on the crucible, which in turn shortens the life of the crucible and increases the amount of zirconium introduced into the sample. In general, the crucible and its contents will come to red heat within about 3 min. The melt in the crucible should then be swirled and the bottom examined for sample particles. The fusion is assumed complete when no more sample particles can be found. Some samples are not so easily distinguished, and only experience with that sample type can form a basis for judging completion.

Sodium peroxide fusions should not be attempted outside a fume hood. At the minimum, an operator should wear safety glasses and a lab coat or apron. Durable gloves would be advisable if samples known to be prone to autofusion are to be used.

APPENDIX C.–NOTES ON SAMPLE PREPARATION

The grind size or mesh size of the sample is an almost crucial consideration in the analysis of mineral chromite, ferrochrome slags, and ferrochrome metal. In general, the finer the sample particle size, the easier it will be to dissolve. If all samples could be ground to pass a 200-mesh screen, nearly all of the dissolution problems would be solved. In practice, a sample ground to pass a 100-mesh screen will present little in the way of problems, but for mineral and slag samples in particular, larger sample particles should be avoided. Larger sample particles of metal, instead of being harder to fuse, are actually easier to fuse but have a tendency to produce hot spots in the crucible and so contribute to burnthrough. Larger metal particles, of course, are slower to dissolve in acid than smaller particles. As a general rule, any sample ground to pass a 100-mesh screen should be acceptable, and any sample that will not pass a 60-mesh screen will present problems with sample decomposition.

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